

DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS

George K. Burgess, Director

---

TECHNOLOGIC PAPERS OF THE BUREAU OF STANDARDS, No. 317

[Part of Vol. 20]

---

# ACTION OF SODIUM SULPHATE IN SYNTHETIC TANNING MATERIALS

BY

EDWARD WOLESENSKY, Chemist

*Bureau of Standards*

---

May 20, 1926



PRICE, 10 CENTS

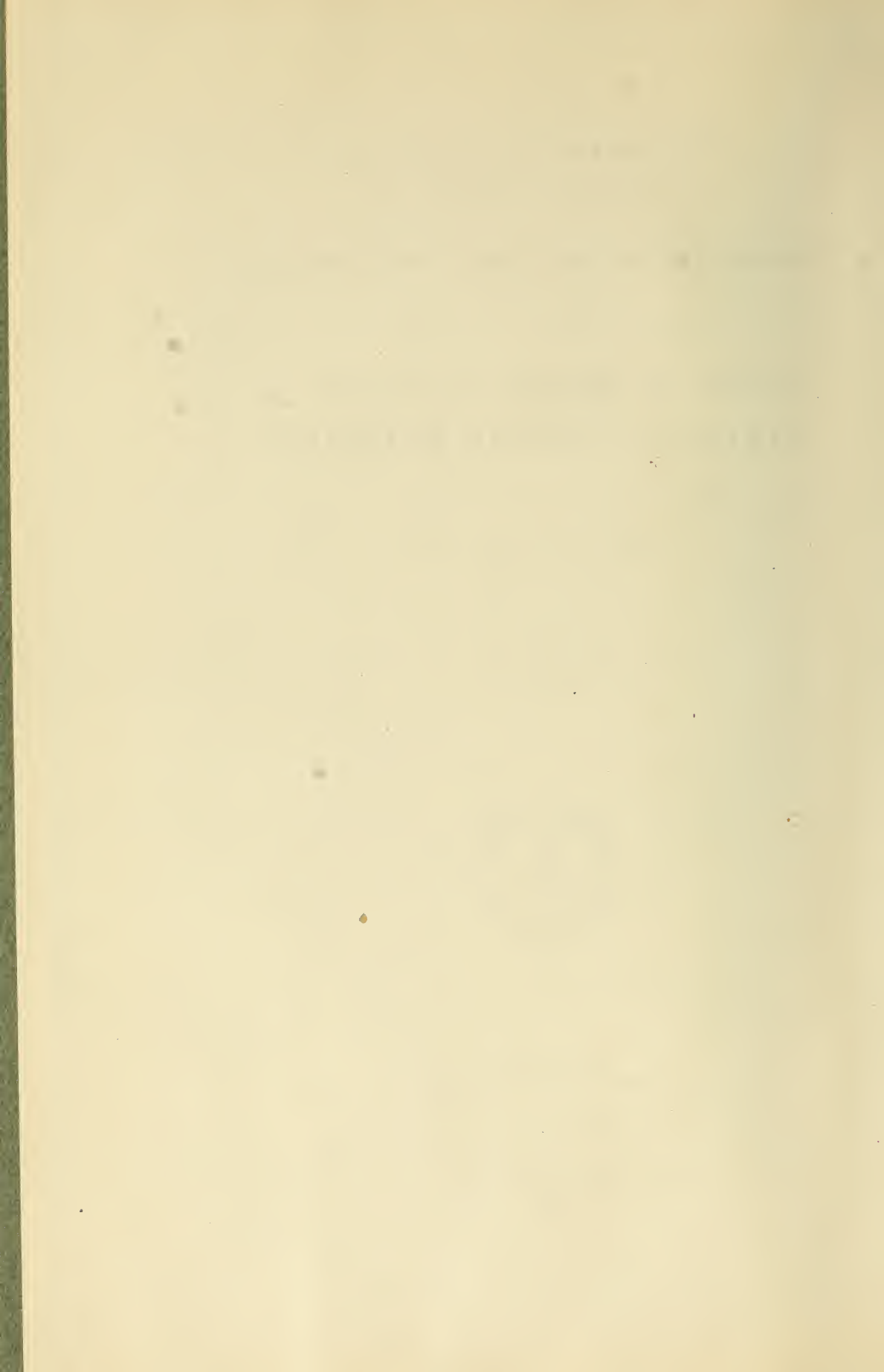
\$1.25 PER VOLUME ON SUBSCRIPTION

Sold only by the Superintendent of Documents, Government Printing Office  
Washington, D. C.

---

WASHINGTON  
GOVERNMENT PRINTING OFFICE

1926



# ACTION OF SODIUM SULPHATE IN SYNTHETIC TANNING MATERIALS

By Edward Wolesensky

## ABSTRACT

Hide substance has such a marked affinity for sulphuric acid that it will absorb the acid from a solution of sodium sulphate acidified with acetic acid. The sulphuric acid so absorbed can not be removed even by prolonged washing, the hide substance retaining 1.4 per cent of its weight of the acid after 72 hours' washing with distilled water.

Furthermore, the sulphuric acid so combined with hide protein can not be completely displaced by a synthetic tanning material, although the latter can itself be partly displaced from combination with the hide substance by sulphuric acid on treatment with a dilute solution of sodium sulphate acidified with acetic acid. Hence, if a hide is treated with a syntan containing a soluble sulphate, it will absorb both sulphuric acid and the synthetic tanning material to a certain extent, depending on the nature of the syntan and the concentrations of the reagents in the tanning bath.

These results apply to the particular syntans studied, and in the absence of other tanning materials. It is also possible that sulphuric acid so combined with the hide protein in leather may not be injurious to the latter.

This behavior of soluble sulphates in synthetic tanning materials will also lead to error in the determination of tanning material and nontannins in the analysis of syntans containing soluble sulphates, by methods involving the use of hide powder.

## CONTENTS

	Page
I. Introduction.....	529
II. Experiments and results.....	531
1. Absorption of free sulphuric acid by hide substance.....	531
2. Absorption of sulphuric acid from sodium sulphate in presence of an acid.....	532
3. Displacement of combined sulphuric acid by syntan.....	536
4. Displacement of combined syntan by sulphuric acid.....	540
III. Summary and conclusions.....	543

## I. INTRODUCTION

In the manufacture of synthetic tanning materials, such as the sulphonated condensation products known as syntans, the unchanged sulphuric acid remaining after sulphonation is not generally removed by precipitation or otherwise, but is usually neutralized in the final product by simply adding the requisite amount of sodium hydroxide or carbonate. Thus the sulphuric acid remains in the solution of syntan in the form of its sodium salt, and in some cases,

possibly all, this is present in very considerable quantities. Now the actual tanning materials in these syntans (sulphonic acids) are generally active acids, many of them, in fact, approaching sulphuric acid itself in activity. Hence, we must expect that even though we add sodium hydroxide or carbonate in an amount chemically equivalent to the unchanged sulphuric acid present, or even more, there will still always be some free sulphuric acid in the solution as long as there is any free sulphonic acid present. The question, therefore, naturally arises as to what will be the behavior of the sodium sulphate toward hide substance in the presence of the sulphonic acid when a hide is suspended in a solution of such a syntan.

It has long been recognized that free sulphuric acid is capable of combining with the protein of hide or leather, but there has always been, and still appears to be, considerable difference of opinion as to the exact nature and stability of this combination, and we have little information as to the extent of this combination or the conditions under which it may take place. Thus Eitner<sup>1</sup> found that the sulphuric acid in leather may be bound to the organic matter of the leather as well as to the mineral matter, and he regarded both forms of combination as harmless to the leather, only the free sulphuric acid being harmful. Procter<sup>2</sup> considered that an actual compound is formed when an acid acts on hide, its nature being that of a salt in which the hide acts as a weak base. But he regarded the combination as a very loose one, the salt being easily hydrolyzable and in equilibrium with the uncombined hide and the acid solution. According to this view it would be impossible to have any sulphuric acid in hide or leather (except in the form of neutral, inorganic salts) without having at least a part of it in the free state. He claimed that the largest amount of acid which can be fixed in the hide is about 1 g equivalent per kilogram of actual hide substance, or about 5 per cent for sulphuric acid, and that most of this acid may be washed out of the hide if enough water is used. Furthermore, he found that when a hide is tanned the combined sulphuric acid is gradually driven out by the tanning, so that the final leather, if completely tanned, may contain practically no sulphuric acid, but if any acid does remain, the durability of the leather is impaired.

Brochet<sup>3</sup> found that the absorption of acids by skins is a general phenomenon, resulting from chemical union of the acid with the hide substance, and that whatever the nature of the acid, the amount absorbed is proportional to its chemical equivalent, although in the case of the less active acids it is slightly less. Immerheiser<sup>4</sup> found that hide and leather have a great affinity for free sulphuric acid, but

<sup>1</sup> Gerber, 794, p. 267; 795, p. 281; 796, p. 296; 797, p. 309; 1908.

<sup>2</sup> Shoe Leather Reporter, 109, p. 31-33.

<sup>3</sup> Compt. rend., 155, pp. 1614-1617.

<sup>4</sup> Collegium, p. 360; 1920.

that this affinity is less in leather than in hide, and that it decreases with characteristic regularity as the tanning process goes on. Jalade<sup>5</sup> also stated that practically all of the acid in leather is chemically combined; but, unlike Procter, he found that very little of this acid can be liberated by hydrolysis on treatment with water, and concluded that the acid content of leather is less important than is generally supposed.

Thus, while there seems to be pretty general agreement among these various investigators as to the formation of a definite chemical compound between the sulphuric acid and the hide substance, there seems to be considerable difference of opinion as to the stability of the compound formed or, in other words, the affinity of the hide substance for the acid. Furthermore, although both Procter and Immerheiser found that the sulphuric acid may be displaced from combination with hide substance by means of vegetable tannin, and we might be led to reason, by analogy at least, that the same thing would take place when the hide is tanned with synthetic tanning materials, we have no direct proof that the latter is actually the case. Finally, the information at hand gives us no clue as to what would take place when the sulphuric acid is present in the form of a soluble sulphate in the presence of hide substance and an active acid. Correct and definite answers to these questions are important not only to the tanner who uses synthetic tanning materials in his process, but also to the analyst in the examination of such materials by the usual methods.

## II. EXPERIMENTS AND RESULTS

### 1. ABSORPTION OF FREE SULPHURIC ACID BY HIDE SUBSTANCE

Some idea of the readiness with which hide substance will remove sulphuric acid from solution may be gained from the following simple experiment. One hundred g of wet, chromed hide powder, containing 73.42 per cent of moisture, were shaken for 10 minutes with 400 cc of approximately one twenty-fifth normal sulphuric acid solution, containing 0.7886 g of actual sulphuric acid. The solution was then separated from the hide powder by first squeezing through a linen bag and then filtering through an ordinary paper filter. Fifty cc of this solution now required 1.48 cc of a 0.10315 N solution of sodium hydroxide for neutralization. Hence the entire solution, having an estimated volume of 473.42 cc, contained 0.07085 g of sulphuric acid after having been in contact with hide powder for only 10 minutes. In other words, over 91 per cent of the original sulphuric acid was removed from the solution by the hide powder in this brief period.

---

<sup>5</sup> Cuir Tech., 13, p. 120.

This alone would indicate a marked affinity on the part of hide substance for sulphuric acid, and would lead one to suspect that the hide substance would probably absorb some sulphuric acid even from a solution of sodium sulphate, in the presence of some other free acid, unless something intervened to prevent this.

## 2. ABSORPTION OF SULPHURIC ACID FROM SODIUM SULPHATE IN PRESENCE OF AN ACID

In order to determine the behavior toward hide substance of sodium sulphate in the presence of an acid, chromed hide powder was first treated with a solution containing about 6 g of anhydrous sodium sulphate and about 5 cc of glacial acetic acid per liter. This concentration of sodium sulphate was selected because it represents about the maximum concentration of this salt that would be encountered in any of the commercial syntans when diluted to "analytical strength," and the amount of acetic acid taken is approximately equivalent (chemically) to the sodium sulphate. One hundred and fifty cc of this solution when evaporated to dryness gave 0.8976 g of residue, dried at 105° C., or 5.984 g per liter.

Two hundred cc of this solution were shaken for 20 minutes with 47.4 g of wet, chromed hide powder containing 72.9 per cent of moisture, and the solution was then separated from the hide powder and filtered as before. One hundred and fifty cc of the filtrate now gave 0.8292 g of dry residue on evaporation. Correcting for the water which was introduced with the hide powder, this would represent 6.482 g of nonvolatile matter per liter of original solution, or an increase of about 8.32 per cent. An increase in nonvolatile matter would be expected if some sulphuric acid had been removed from the solution by the hide powder and replaced in the dry residue by acetic acid, but of course it is also possible that some or all of this increase might be due to material dissolved out of the hide powder by the solution, as was in fact indicated by the grayish color of the residue.

The dry residue from the filtrate was therefore dissolved in a small amount of water, acidified with 20 cc of a 5 per cent solution of phosphoric acid, distilled in a current of steam into standard sodium hydroxide solution (0.1006 *N*), and the distillate titrated with standard sulphuric acid, using phenolphthalein as indicator. It was found that 14.00 cc of the sodium hydroxide had been neutralized by the acid which came over in the distillate, representing 0.08453 g of acetic acid in the residue from 150 cc of filtrate, or 0.6610 g per liter of original solution. This latter quantity of acetic acid is chemically equivalent to 0.7822 g of sodium sulphate, or 13.07 per cent of the original salt, which had been converted to acetate during the treatment with hide powder.

The remainder of the filtrate was evaporated to dryness and the residue dried at  $110^{\circ}$  C. A portion of the residue when treated with alcohol and sulphuric acid gave a distinct odor of ethyl acetate, and another portion when heated with dry arsenious anhydride gave a distinct odor of cacodyl oxide, thus giving positive proof of the presence in the residue of combined acetic acid.

The results would thus seem to demonstrate in a most striking manner the affinity of hide substance for sulphuric acid. But, in order to obtain additional data, as well as to eliminate any possible effect of the chromic sulphate, the above experiment was repeated with some modifications. Twenty-five g of air-dried hide powder, containing 12 per cent of moisture, were treated directly (that is, without previous chroming) with 500 cc of a solution of sodium sulphate and acetic acid similar to that which was used in the above experiment. One hundred cc of this solution on evaporation gave a residue of 0.6155 g. The treatment of the hide powder with this solution was continued for 24 hours, and while the shaking was not continuous during this period, the mixture was shaken frequently. The solution was then separated from the hide powder as before, and saved for analysis, while the hide powder itself was washed by soaking in distilled water for 48 hours, with frequent shaking, the water being changed 12 times during this period, after which the hide powder was dried for analysis.

One hundred and forty cc of the filtrate evaporated to dryness and dried at  $105^{\circ}$  C. gave a residue of 1.3978 g, or, correcting for the moisture in the original hide powder, 5.0221 g in the entire solution of 503 cc. The dry residue thus obtained was then redissolved in water, acidified with 25 cc of a 5 per cent solution of phosphoric acid, and distilled in a current of steam into a standard solution of sodium hydroxide (0.0971 times *N*), after which the distillate was titrated as before, to determine the amount of acetic acid combined in the residue. It was found that the acetic acid in the distillate had neutralized 26.07 cc of the sodium hydroxide solution, corresponding to 0.2077 g of sodium acetate in 140 cc of the filtrate, or 0.7461 g in the entire solution.

One hundred and fifty cc of the filtrate were treated with excess of sulphuric acid, concentrated to small bulk, and then digested with concentrated sulphuric acid for a determination of organic nitrogen by the Kjeldahl method. The ammonia obtained in the subsequent distillation was found to have neutralized 59.17 cc of a 0.10095 times normal sulphuric acid solution, indicating 0.4698 g of hide substance in the 150 cc of filtrate, or 1.5754 g in the entire solution.

Seventy-five cc of the filtrate were treated with some nitric acid, evaporated to dryness, and the residue digested for about five hours

with hot, concentrated nitric acid. The solution was then concentrated to small bulk, diluted with water, treated with barium chloride solution, and the precipitated barium sulphate filtered off, washed, dried, ignited, and weighed. The weight of barium sulphate was found to be 0.6593 g, representing 0.4012 g of sodium sulphate in the 75 cc of filtrate, or 2.6909 g in the entire solution.

Summarizing these results, we find that the entire solution, having an estimated volume of 503 cc after being in contact with the hide powder for 24 hours, contained the following:

Sodium sulphate.....	2. 6909
Sodium acetate.....	. 7461
Hide substance.....	1. 5754
Total.....	5. 0124
Residue actually found.....	5. 0221

The hide powder, which was removed from the solution, after having been washed and dried as described above, was analyzed for total sulphur as follows: A sample of the hide powder (dried at 105° C.) was dissolved in concentrated nitric acid and the solution gently heated for about eight hours. After standing overnight this solution was evaporated to small bulk, diluted with water, and the sulphuric acid precipitated with barium chloride as before. The results of two duplicate analyses were as follows:

	I	II
Weight of hide powder.....grams.....	4. 4361	4. 2562
Weight of barium sulphate.....do.....	. 1195	. 1081
Sulphur.....per cent.....	. 370	1. 349

<sup>1</sup> It is not customary in giving analytical data to calculate percentages to the third decimal; in fact, in most cases the error may be as much as one or more units in the first decimal. In the present work, however, owing to the fact that small differences were being considered, it was necessary to obtain a higher degree of accuracy in analysis than is usual, and this, it is believed, was accomplished by taking large samples for analysis (approximately 5 g of leather or hide substance). Furthermore, it must be noted that the sulphur content is generally reported as such, although it was actually weighed in the form of barium sulphate, which is about 7.28 times as heavy as the sulphur which it contains, so that the absolute error in the determination of the barium sulphate was decreased in this ratio when the results were calculated to sulphur. As a matter of fact, it was found very easy to obtain duplicate determinations of sulphur agreeing within 0.05 per cent, and differences of 0.02 or 0.03 per cent or less were not uncommon. Hence, it is considered justifiable in this work to carry the percentages of sulphur to three decimal places.

The sulphur content of the original hide powder (after drying at 105° C.) was also determined in the same way, with the following results:

	I	II
Weight of hide powder.....grams.....	5. 0929	4. 6431
Weight of barium sulphate.....do.....	. 0204	. 0173
Sulphur.....per cent.....	. 055	. 051

The average content of total sulphur in the final hide powder was, therefore, 0.36 per cent, while the average content of sulphur in the original hide powder was 0.053 per cent, leaving a balance of 0.307 per cent, which represents the sulphur absorbed from the solution in the form of sulphuric acid.

In an attempt to determine whether or not the content of sulphuric acid in the hide powder can be increased, 30 g of air-dry hide powder were treated for 24 hours with 600 cc of the sodium sulphate-acetic acid solution as before, except that a half hour before the end of this treatment 1.68 cc of 95 per cent sulphuric acid were added, making the solution approximately one-tenth normal with respect to the free acid. A higher concentration of free acid and longer treatment with the same were not considered desirable on account of the excessive plumping action on the hide powder, which would make subsequent washing very difficult. After washing with distilled water for 48 hours as before, the hide powder was again analyzed for total sulphur, with the following results:

	I	II
Weight of hide powder.....grams..	4.0666	4.1595
Weight of barium sulphate.....do.....	.1161	.1192
Sulphur (total).....per cent.....	.392	.393

Comparing these results with those obtained in the previous experiment, we see that the content of total sulphur is here slightly higher, but not materially so.

A double treatment with the sodium sulphate-acetic acid solution was next tried; that is, after treating the hide powder with one portion of the solution for 24 hours it was separated from the solution by squeezing in a linen bag and then placed, without washing, into another fresh portion of the same solution for a period of 48 hours, after which it was washed as before, but for a period of 72 hours instead of 48 (the water being changed 15 times), then dried and analyzed for total sulphur. This time there was a considerable increase in the total content of sulphur (and, therefore, of combined sulphuric acid) as is shown by the following results:

	I	II
Weight of hide powder.....grams..	4.7637	4.7776
Weight of barium sulphate.....do.....	.1778	.1754
Sulphur (total).....per cent.....	.512	.504

Correcting for the sulphur content of the original hide powder (0.053 per cent), the average amount of sulphur combined as sulphuric acid is 0.455 per cent, or about 50 per cent increase over the proportion found combined in the first case above. While no at-

tempt was made to determine the limiting proportion of sulphuric acid that can be made to combine with hide substance in this way, considering all of the facts mentioned above it is evident that although the first portion of sulphuric acid is taken up from the solution very quickly, the rate of reaction drops off rapidly, and the limit is approached very slowly. It is also probable that the maximum quantity of sulphuric acid which can combine with the hide substance, under the above conditions, so firmly that it can not be washed out with water in any reasonable length of time, is not much higher than the amount indicated in the last results given above, which correspond to about 1.4 per cent as sulphuric acid.

But the most important point brought out in the experiments just described is the fact that hide substance is capable of removing sulphuric acid from soluble sulphates in the presence of even so weak an acid as acetic. It is a foregone conclusion, therefore, that it will also do so in the presence of more active acids, such as most of the sulphonic acids are. It remains to be shown, however, whether this can take place in the presence of an active tanning agent, such as most of the syntans are, whether this tanning agent is capable of displacing sulphuric acid which is already combined with the hide substance, or whether the tanning agent itself can be displaced from combination with the hide substance by sulphuric acid.

### 3. DISPLACEMENT OF COMBINED SULPHURIC ACID BY SYNTAN

To determine whether or not sulphuric acid which is already combined with hide substance can be displaced by a syntan, some standard hide powder was first treated with a solution containing sodium sulphate and acetic acid, then tanned with a syntan (which also contained some sodium sulphate), and, after thoroughly washing, analyzed for total sulphur. The result obtained was then compared with that obtained by tanning another portion of the hide powder in the same manner as before, but without previously treating it with the sodium sulphate-acetic acid solution, and using the same syntan but without free sulphuric acid or soluble sulphate.

The syntan used in this experiment was prepared by first sulphonating 2 moles of phenol with about 2.2 moles of sulphuric acid, dissolving the sulphonation mixture in water and heating for two hours at 90 to 100° C. in a tightly closed vessel with about 1.05 moles of a 37.5 per cent solution of formaldehyde. The resulting solution, after filtering, contained 30.2 g of free sulphuric acid and 142.8 g of tanning material, the latter being determined by the official method of the American Leather Chemists' Association, after first precipitating the free sulphuric acid by adding the equivalent quantity of barium acetate. Hence, when the solution was treated with sodium hydroxide equivalent to the free sulphuric acid present, the ratio of sodium sulphate to tanning material in the solution was 1:3.26.

Twenty g of hide powder (air-dried) were treated for 24 hours with 400 cc of a solution of sodium sulphate and acetic acid of about the same concentrations as those already described, viz, 6 g of anhydrous sodium sulphate and 5 cc of glacial acetic acid per liter.<sup>6</sup> During this treatment the mixture was frequently shaken. Then, without removing the sodium sulphate-acetic acid solution, a quantity of the above-described syntan was added containing 2.5 g of actual tanning material (the free sulphuric acid being neutralized with NaOH) and diluted with enough water to make the volume of the entire solution, exclusive of the hide powder, equal to 500 cc. This was shaken continuously for an hour. The solution was then separated from the hide powder by squeezing through a linen bag and replaced with 500 cc of the same syntan but of double the first concentration, and again shaken for an hour. Finally, the solution was again replaced by one of the same syntan of four times the original concentration for 20 hours, with intermittent shaking. The concentrations of the successive solutions of syntan used in this treatment were thus approximately 0.5, 1, and 2 per cent, respectively. After again separating from the solution, the tanned hide powder was now washed for 48 hours with distilled water, changing the water 12 times during this period, and shaking frequently meanwhile. Finally it was dried and analyzed for total sulphur in the same manner as in previous experiments, with the following results:

	Per cent of total sulphur
I.....	2.745
II.....	2.728
Average.....	2.736

Another portion of hide powder was simultaneously tanned in the same manner with the same syntan, but without previously treating the hide powder with the sodium sulphate-acetic acid solution, and using a solution of syntan from which the free sulphuric acid had previously been removed by adding an equivalent quantity of barium acetate. The bulk of the barium sulphate was separated from the syntan solution by settling and decantation, but since it settled very slowly some of it remained suspended in the solution when the latter was used in tanning the hide powder, and adhered to the tanned hide powder so firmly that it could not be washed out during the subsequent washing. After determining the total sulphur in the final product, therefore, the amount present in the form of

<sup>6</sup> Since a solution of approximately the same composition was used throughout this work, it will be merely referred to hereafter as the "sodium sulphate-acetic acid solution."

adhering barium sulphate had to be determined separately and a correction made for the same. The results obtained in this case are as follows:

	I	II	Average
Sulphur (total).....per cent..	2.890	2.862	2.876
Sulphur in form of barium sulphate.....do.			.066

Correcting the total sulphur content of the leather for that present as barium sulphate, we find that the total sulphur content of the barium sulphate-free hide powder is 2.812 per cent as compared with 2.736 per cent for the hide powder which had been subjected to the action of sodium sulphate and acid. The difference, 0.076 per cent, is not large, but it is too large to be accounted for as experimental error in the determination of the sulphur. Furthermore, the difference is in the direction in which we would expect it to be if in the one case the hide powder contained combined sulphuric acid which the tanning material failed to displace in whole or in part, assuming that both the sulphuric acid and the tanning material (sulphonic acid) are combined with the hide protein through the amino groups of the latter and bearing in mind that the sulphuric acid is a dibasic acid while the sulphonic acid is monobasic. Under these conditions the hide powder containing combined sulphuric acid would contain less total sulphur than the hide powder in which the amino groups were combined to the same extent with sulphonic acid only.

The small amount of the difference actually observed in the above experiment might indicate that only a small amount of combined sulphuric acid was present, or it might be due to the fact that the hide powder was not completely saturated with acid (either sulphuric or sulphonic) in either or both cases. The experiment was therefore repeated with the same materials and in exactly the same manner except that during the tanning process the hide powder was given an additional treatment for 48 hours with the 2 per cent solution of syntan. In other words, each portion of hide powder (one being previously treated with the sodium sulphate-acetic acid solution) was first treated with a 0.5 per cent solution of syntan for 1 hour, then with a 1 per cent solution for 1 hour, then with a 2 per cent solution for 24 hours, and finally with a fresh portion of the 2 per cent solution for another 48 hours. After washing and drying as before, the following percentages of total sulphur were found in the two portions of hide powder, the one which received the preliminary treatment with the sodium sulphate-acetic acid solution being designated by (a) and the one which was treated only with the syntan free from sulphuric acid or soluble sulphate being designated by (b).

	I	II	Average
a.....	2.768	2.747	2.757
b.....	3.063	3.102	3.082

The sulphur present in (b) as adsorbed barium sulphate amounted to 0.058 per cent of the weight of the sample. Correcting for this, the total sulphur in the barium sulphate-free leather was 3.037 per cent, or an increase of 0.280 per cent over that which had first been treated with the sodium sulphate-acetic acid solution and subsequently with syntan containing some more sodium sulphate. On the other hand, the latter contains practically the same amount of total sulphur as in the preceding experiment in which it was given a shorter treatment with the syntan. These results can leave no doubt that the sulphuric acid which was allowed to combine with the hide substance previous to tanning was not displaced by the tanning material subsequently, or was displaced only in part.

Experiments similar to the above were also carried out with a syntan of a somewhat different type. This syntan was prepared by first condensing cresylic acid (2 moles) with formaldehyde (1 mole) by heating at 90 to 100° C. for two hours in a tightly closed vessel in the presence of a 25 per cent solution of sulphuric acid, washing and drying the resin so obtained, and then sulphonating it with concentrated sulphuric acid (95.13 per cent), using 1 part of the latter to 1.48 parts of the resin. The product when dissolved in water and analyzed was found to contain 39.97 g of free sulphuric acid and 248.57 g of tanning material, so that when treated with sodium hydroxide in a quantity equivalent to the unchanged sulphuric acid it would contain 1 part of sodium sulphate to 4.29 parts of tanning material.

Owing to the fact that this type of syntan, as has been shown in another study,<sup>7</sup> combines with hide substance to a greater extent and requires longer time to reach maximum combination, the treatment of the hide powder with the syntan was lengthened somewhat, the periods allowed for each concentration being as follows: 1 hour with 0.5 per cent solution, 1 hour with 1 per cent solution, 2 days with the 2 per cent solution, and a second period of 2 days with a fresh portion of the 2 per cent solution. The products were then washed, dried, and analyzed for total sulphur as before. Again designating the hide powder which had received preliminary treatment with the sodium sulphate-acetic acid solution by (a) and that which had been treated with syntan free from sulphuric acid or sulphate by (b), the per cent of total sulphur found was as follows:

	I	II	Average
a.....	2.211	2.197	2.204
b.....	2.558	2.548	2.553

<sup>7</sup> B. S., Tech. Paper No. 309.

The amount of sulphur present in (b) as adsorbed barium sulphate was found to be 0.217 per cent, so that the total sulphur content of the barium sulphate-free leather was 2.341 per cent. This is 0.137 per cent higher than in the leather which had been treated with the sodium sulphate-acetic acid solution previous to tanning, and shows that here again the syntan failed, either wholly or in part, to displace the sulphuric acid already in combination with the hide substance.

#### 4. DISPLACEMENT OF COMBINED SYNTAN BY SULPHURIC ACID

In order to determine whether or not sulphuric acid is capable of displacing a syntan already in combination with hide substance, a number of leathers which had been tanned with various syntans, thoroughly washed and analyzed for total sulphur, were subjected to the action of a sodium sulphate-acetic acid solution, and then again thoroughly washed and analyzed for total sulphur. In the first three experiments (see following table) the hide was tanned in the whole (not ground) condition, the tanning being carried out in the usual manner, starting with a solution of about 0.5 per cent concentration, raising this gradually to a concentration of about 5 per cent in the course of a week, and continuing the tanning for a total of about three weeks. The leathers so obtained were then washed in running water for about 8 hours, allowed to dry for about a week, then ground into a powder and washed again in distilled water for 48 hours in the manner already described in an earlier part of this work; that is, simply allowing the powder to soak in the water with frequent shaking and changing the water 12 times during this period. In these first three experiments the solutions of the syntans contained the sodium sulphate normally present from the neutralization of the unchanged sulphuric acid. In the last two experiments, the last two hide powders which had been tanned with the sulphate-free syntans (see preceding section of this paper, pp. 538 to 539) for determining the power of syntans to displace combined sulphuric acid were used, the leather used in experiment 4 being the one which had been tanned with the syntan derived from phenolsulphonic acid, and the one in experiment 5 having been tanned with the syntan derived from the cresylic acid-formaldehyde resin. The syntan used in experiment 1 was derived from phenolsulphonic acid in much the same manner as the one used in experiment 4 except that the condensation of the formaldehyde with the sulphonie acid was carried out in concentrated solution and at a temperature of 25 to 30° C., whereas the syntan used in experiment 4 had been condensed in dilute solution and at elevated temperature. The syntan used in experiment 2 was prepared by first condensing phenol with paracetaldehyde in the presence of a small amount of sulphuric acid, and then sulphonating the result-

ing resin, while the syntan used in experiment 3 was prepared like that used in experiment 5, but represented a different preparation. The treatment with the sodium sulphate-acetic acid solution was continued in each case for 72 hours, and was carried out exactly as similar treatments described in preceding experiments. The proportion of sodium sulphate-acetic acid solution to leather taken was in all cases 500 cc of solution to 24 g of air-dried leather. The second washing (following the treatment with the sodium sulphate-acetic acid solution) was carried out exactly like the previous washing and likewise lasted for 48 hours. The results are given in the following table. In experiments 4 and 5, the averages are corrected for the sulphur present as adsorbed barium sulphate. (Incidentally it may be pointed out that the amount of this adsorbed barium sulphate in the leather was not appreciably decreased by the prolonged treatment with the sodium sulphate-acetic acid solution and the subsequent washing, thus showing how firmly it was fixed in the leather.)

TABLE 1

Experiment	Determination	Total sulphur in original leather	Total sulphur in final leather	Difference
		<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
1.....	I.....	2.781	2.661	0.120
	II.....	2.033	1.896	-----
2.....	II.....	2.037	1.873	-----
	Average.....	2.035	1.884	.151
	I.....	2.103	1.970	-----
3.....	II.....	2.157	1.969	-----
	Average.....	2.130	1.970	.160
	I.....	3.063	2.810	-----
4.....	II.....	3.102	2.870	-----
	S as BaSO <sub>4</sub> .....	.058	.063	-----
	Average (corrected).....	3.037	2.779	.258
	I.....	2.558	2.467	-----
5.....	II.....	2.548	2.458	-----
	S as BaSO <sub>4</sub> .....	.217	.215	-----
	Average (corrected).....	2.341	2.252	.089

In every case there was an appreciable decrease in the content of total sulphur, and the difference is too large to be attributable entirely to experimental error. If the latter were the correct explanation of the differences it is not likely that all of the errors would be in the same direction. The differences noted are, at least qualitatively, exactly what we should expect if 1 molecule of the dibasic sulphuric acid displaced 2 molecules of sulphonie acid from combination with the hide substance.

Another consequence of such a displacement would be an increase in the total sulphur content of the sodium sulphate-acetic acid solu-

tion. Such a result was actually observed. In each of the experiments of the last series the sodium sulphate-acetic acid solution was filtered from the leather, a measured portion of the filtrate was treated with concentrated nitric acid and evaporated to dryness. The residue was then further digested with concentrated nitric acid to oxidize any organic matter, and the total sulphur in the residue determined by precipitation as barium sulphate, as in preceding experiments. The results, as well as the total sulphur content of the original solution (calculated as sodium sulphate in both cases), are given in Table 2.

TABLE 2.—Total sulphur as  $\text{Na}_2\text{SO}_4$  in grams per 100 cc

Experiment	Original	Final	Difference
1 -----	0.6037	0.6245	0.0208
2 -----	.6053	.6243	.0190
3 -----	.6053	.6270	.0217
4 -----	.6080	.6458	.0378
5 -----	.6080	.6175	.0095

Finally, a part of the filtrate from the leather in each case was evaporated to dryness and the residue dried for two or three hours in an oven at  $110^\circ \text{C.}$ , to drive off all acetic acid. The residue was then taken up in distilled water and tested for acidity. In all cases the residue was distinctly acid toward litmus, and in some cases it was even distinctly, though faintly, acid toward Congo red, showing that there was an excess of a mineral acid. This is again precisely what we should expect if 1 molecule of sulphuric acid displaced 2 molecules of sulphonic acid from combination with the hide substance, and the latter acid were subsequently hydrolyzed during evaporation.

All of these results could also be explained if we assumed that the loss of total sulphur content of the leather, as shown in Table 1, was due merely to washing out of the syntan, without any chemical action due to the presence of the sodium sulphate and acetic acid. This, however, would also require the assumption that the hide-syntan compound is not very stable and that the syntan would continue to be washed out of the leather practically indefinitely, or at least that a stable condition toward water can not be reached within 48 hours of washing (the first washing in the above experiments). That such was not the case, however, is shown by the following experiments.

Four different leathers which had been tanned with the same syntans as were used in the experiments of the last series above with the exception of experiment 2, after being washed in the disintegrated condition for 48 hours as in preceding experiments, and then analyzed for total sulphur, were given a second washing with distilled water in the same manner as before for a period of 72 hours and again analyzed for total sulphur. It should be noted, however, that in the

present series of experiments all of the syntans contained the sodium sulphate normally resulting from the neutralization of the unchanged sulphuric acid. The results are given in Table 3, the experiments being numbered so as to correspond with those in Tables 1 and 2, in which the same syntans were used.

TABLE 3.—*Percentage of total sulphur in leather*

Experiments	After first washing	After second washing	Difference
1.....	2.799	2.805	0.006
3.....	2.130	2.079	.051
4.....	2.757	2.728	.029
5.....	2.204	2.258	.054

It will be observed that the results after the second washing differ very little from those after the first washing, and that in two cases the difference is an increase while in the other two cases it is a decrease. Evidently, then, within the limits of experimental error there has been no decrease in the sulphur content of the leathers involved during the second period of washing. We must therefore conclude that leathers which have been prepared with such tanning materials as those here used have reached a stable condition when washed for 48 hours in the manner adopted in this work, and further washing will not result in any change in composition of such leathers. Hence, we must also conclude that the losses in total sulphur content which have been noted in Table 1 are due, not to a washing out of syntan, but to the chemical action of the sodium sulphate in the presence of acetic acid, or, in other words, to the displacement of the syntan by sulphuric acid.

### III. SUMMARY AND CONCLUSIONS

It has been shown that sulphuric acid and hide substance are not only capable of entering into actual chemical combination with each other, but that the affinity between the two is so pronounced that hide substance is capable of removing sulphuric acid even from a dilute solution of sodium sulphate acidified with acetic acid (approximately 0.5 per cent of each). Furthermore, the sulphuric acid thus combined in the hide substance is so firmly bound that it can not be removed completely even on prolonged washing with water at ordinary temperatures. The amount of the acid which may remain combined with the hide substance after washing with water for 72 hours is at least 1.4 per cent of the weight of the hide substance.

It has also been shown that sulphuric acid when once combined with hide substance can not be completely displaced by a syntan, but that, on the other hand, the syntan itself can, to a certain extent, be displaced from combination with hide substance by means of sul-

phuric acid, even though the latter is present only in the form of its sodium salt in dilute solution acidified with acetic acid.

It therefore follows that if a hide is treated with a solution containing both sodium sulphate and a synthetic tanning material (which is usually an active acid) both the sulphuric acid and the tanning material will combine with the hide to a certain extent. In other words, the neutralization of the excess sulphuric acid in syntans, by means of sodium hydroxide or any other reagent which yields a soluble sulphate, does not entirely prevent the sulphuric acid from reacting with the hide during the tanning process. The extent to which the sulphuric acid and the synthetic tanning agent will combine with the hide under these conditions is not yet definitely known, but it is probable that an equilibrium will ultimately be reached, depending partly on the nature of the syntan and partly on the concentrations of the reagents in the tanning solution. But whatever the amount of the sulphuric acid which will be combined in the leather, the results obtained in the present study indicate that this can not be completely removed by any amount of washing with water at ordinary temperatures. It is possible and even probable that this combined sulphuric acid which remains in the leather after thorough washing will have no injurious effect on it, but this still remains to be definitely ascertained. In any case, thorough washing of the leather after using a syntan which contains any considerable amount of sodium sulphate or other soluble sulphate is always necessary in order to prevent injury from the free sulphuric acid which would result from the interaction of the sulphate with any excess of uncombined sulphonc acid.

On the other hand, if a hide removes sulphuric acid from a solution containing sodium sulphate and a sulphonc acid, it is evident that some of the sulphonc acid (a tanning material) must be left behind in the form of its sodium salt (which is not a tanning material) to take the place of the sulphuric acid which was removed by the hide. This would certainly be objectionable if it occurred to any considerable extent.

Finally, this behavior of sodium sulphate in syntans must result in appreciable error in the determination of the "nontannins" (and therefore of tanning material) in such products by any method involving the use of hide powder, not only because sulphuric acid is absorbed by the hide powder and therefore classed as tanning material, but also because an equivalent amount of sulphonc acid is left behind and classed as "nontannin." This difficulty, however, may be overcome by first precipitating all free sulphuric acid or soluble sulphates from the syntan solution by the addition of an equivalent quantity of barium acetate. If the resulting barium sulphate can not be removed before the treatment with hide powder, a correction can easily be made for it afterwards.

WASHINGTON, January 28, 1926.





